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Mechanism of formation of thermoelectric layered cobaltates by annealing CaO-CoO thin films grown by reactive sputtering

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Thermoelectricity requires materials with high thermopower and low electrical resistivity simultaneously with low thermal conductivity. Good thermoelectric materials are usually crystalline materials having structural features that can act as scattering centers for phonons to minimize thermal conductivity, however with no significant disruption in electronic transport; this is referred to as a 'phonon-glass electron-crystal'[1]. In this regard, layered materials, particularly layered cobalt oxides, have drawn much attention of research communities. Isolated CoO_2 layers are unstable in nature and it is stable when CoO_2 layers are separated by a single plane of alkaline metal ions, like $(Na/Ca)_xCoO_2$ (with $0 < x < 1$) [2], or otherwise separated by rock-salt structured $[Ca_2CoO_3]$-block like $[Ca_2CoO_3]_q[CoO_2]$ with $0.5 < q < 1$ (Here, $[Ca_2CoO_3]$-block, acting as blocking layer for phonon, and CdI_2-type hexagonal $[CoO_2]$-block, acting as conducting channel for electron, stack alternatively along c-axis). With such inherent layered structure this class of materials is anisotropic in nature and can serve the same purpose as 'phonon-glass electron-crystal'. $Ca_3Co_4O_9$, also represented as $[Ca_2CoO_3]_{0.62}CoO_2$, is the most studied compound in the family of layered cobaltates. Best thermoelectric performance has been reported to be exploited from its single crystalline form [3]. However, huge technical challenges are associated with the growth of larger dimension of single crystalline $Ca_3Co_4O_9$ required for practical realization of thermoelectric devices. An alternative, approach could be the growth of highly textured and epitaxial thin films. Here, we report a novel two step sputtering/annealing method for the formation of highly textured Ca_xCoO_2 (x=0.47) and $Ca_3Co_4O_9$ thin films [4]. CaO-CoO films are first deposited by reactive magnetron co-sputtering from metallic targets of Ca and Co and then annealed to obtain the final phase. The *in-situ* time-resolved annealing experiments using synchrotron-based XRD as well as *ex-situ* annealing experiments revealed that the thermally induced phase transformation into $Ca_3Co_4O_9$ consists of three steps as shown in Fig. 1. Highly textured $Ca_3Co_4O_9$ thin films exhibit good thermoelectric properties and leaves scope for further improvement by ensuring uniform distribution of CaO and CoO phases in the as-deposited film, e.g., by sequential deposition. The sputtering/annealing method may also be employed for the growth of other layered cobalt oxide compounds and, presently, it is being examined for the growth of Ca_2CoO_5 (also represented as $[Ca_2CoO_3]_1CoO_2$) thin films.

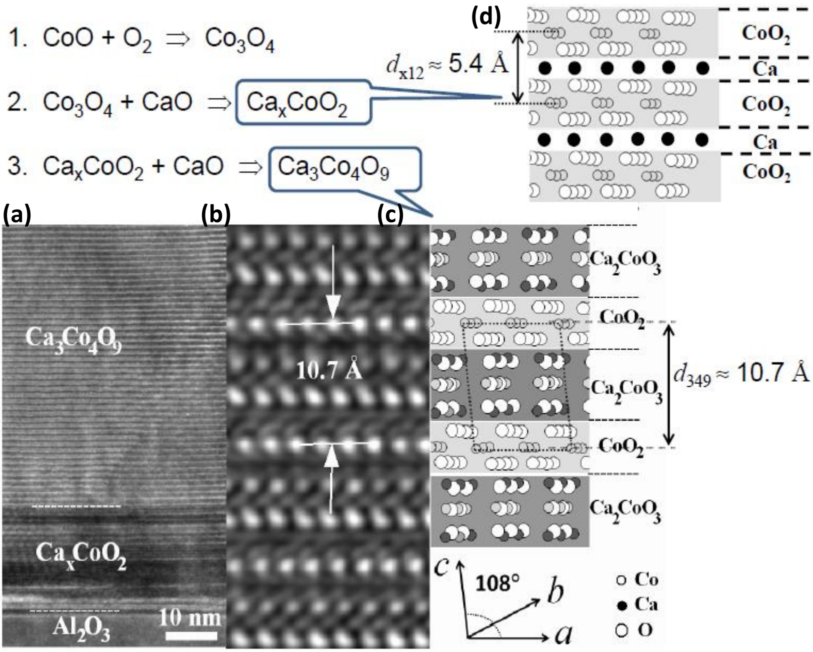

Figure 1: *(a) A typical TEM image showing the layered structure of $Ca_3Co_4O_9$ thin films. About 10 nm interfacial regions consist of Ca_xCoO_2, which is attributed to Ca deficiency in interfacial region of as-deposited CaO-CoO film. (b) HRTEM image shows the periodicity of $Ca_3Co_4O_9$ layers 10.7 Å, whereas the periodicity of Ca_xCoO_2 layers is found to be around 5.4 Å. (c) and (d) Schematic representation of atomic arrangements of $Ca_3Co_4O_9$ and $Ca_{0.47}CoO_2$ layers, respectively.*

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